

**HYBRID MEMBRANES FOR SEPARATE HYDROGEN SULFIDE (H_2S) GAS
FROM REFINERY WASTEWATER TREATMENT**

FOO CHEE YEW

**A thesis submitted in fulfillment
of the requirements for the award of the Degree of
Bachelor of Chemical Engineering (Gas Technology)**

**Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang**

DECEMBER 2010

ABSTRACT

The objective of this research is to separate hydrogen sulfide (H_2S) gas from refinery wastewater treatment and study the influence of composition on the membrane performance for wastewater treatment. Membranes with monosodium glutamate (MSG) as an additive have been fabricated. Four dope solutions with 22% polyamide and different ratio of formic acid /MSG has prepared. The performance of membranes is evaluated based on eight parameters. There are flow rate, turbidity, Chemical oxygen demand (COD), Biochemical oxygen demand (BOD), pH, sulfide, conductivity and Total dissolve substances (TDS). The results show that membrane with 5% of MSG giving the better results. A hybrid membrane has high effectiveness in wastewater treatment. It have been reduced the turbidity, Chemical oxygen demand (COD), Biochemical oxygen demand (BOD), pH, sulfide, conductivity and Total dissolve substances (TDS) values for refinery waste water to the accepted level and achieve the requirement for standard A and B.

ABSTRAK

Tujuan projek ini dijalankan adalah bagi memisahkan gas hidrogen sulfurik (H_2S) daripada air kumbahan yang berasal dari kilang penapisan. Selain itu, projek ini juga mengkaji impak komposisi ke atas prestasi membrane dalam sistem perawatan air kumbahan. Membrane dengan bahan tambahan iaitu monosodium glutamate (MSG) atau ajinomoto telah disediakan. Empat jenis cecair membrane yang berbeza dari segi komposisi telah disediakan. Composisi cecair tersebut adalah 22% poliamide bersama dengan nisbah yang berbeza bagi asid formik dan MSG. Prestasi membrane telah dinilai daripada lapan parameter yang berbeza. Antaranya, kadar aliran, kekeruhan air kumbahan, Biochemical Oxygen demand (BOD), Chemical oxygen demand (COD), kuantiti sulfide, konduktiviti dan Total dissolve substances (TDS). Keputusan daripada projek ini menunjukkan bahawa membrane dengan 5% MSG dalam komposisi telah member keputusan yang paling baik. Selain itu, membrane hibrid telah menunjukkan kepekesanan yang tinggi dalam merawat air kumbahan. Hal demikian dibuktikan dengan kadar peurunan yang mendadak bagi nilai kekeruhan air kumbahan, Biochemical Oxygen demand (BOD), Chemical oxygen demand (COD), kuantiti sulfide, konduktiviti dan Total dissolve substances (TDS) sehingga ke tahap yang munasabah serta memenuhi keperluan standard A dan B.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENTS	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	ix
	LIST OF FIGURES	x
	LIST OF ABBREVIATIONS	xi
	LIST OF APPENDIX	xii
1	INTRODUCTION	
	1.1 Background of Study	1
	1.2 Problem Statement	3
	1.3 Objective	4
	1.4 Scope of Study	4
	1.5 Rationale and Significance	4
2	LITERATURE REVIEW	
	2.1 Membrane	5
	2.2 Hybrid membrane	7
	2.3 Membrane additive	8
	2.4 Ultrafiltration (UF) membrane	11
	2.5 Hydrogen Sulfide (H ₂ S)	12
	2.6 Standard A and standard B	16
	2.7 Parameters	18
	2.7.1 Biochemical Oxygen Demand (BOD) / Chemical Oxygen Demand (COD)	
	2.7.2 pH	19
	2.7.3 Conductance or Electrical Conductivity (EC) and Dissolve solid	20
	2.7.4 Turbidity	21
	2.8 Refinery Wastewater	22

3	METHODOLOGY	
3.1	Materials	25
3.2	Experiment Set up	25
3.2.1	Preparation	26
3.2.1.1	Preparing silica sand and activated carbon column	26
3.2.1.2	Preparing membrane	27
3.2.2	Installation Equipment	28
3.2.3	Running experiment	29
3.2.4	System Evaluations	29
3.2.4.1	Flow rate	29
3.2.4.2	Turbidity	30
3.2.4.3	Chemical Oxygen Demand (COD)	30
3.2.4.4	Biochemical Oxygen Demand (BOD)	30
3.2.4.5	pH	31
3.2.4.6	Sulfide	31
3.2.4.7	Conductivity and Total Dissolve Substance (TDS)	31
4	RESULTS AND DISCUSSION	
4.1	Effect of Viscosity For Dope solution	32
4.2	Properties of Raw Refinery Wastewater Sample	35
4.3	Testing By Using Silica Sand Only And Activated carbon only	36
4.4	Testing By Using Combine Silica Sand And Activated carbon	37
4.5	Testing For Membrane Performances	38
4.5.1	Flow Rate	39
4.5.2	Turbidity	38
4.5.3	Chemical Oxygen Demand (COD)	40
4.5.4	Biochemical Oxygen Demand (BOD)	42
4.5.5	pH	43
4.5.6	Sulfide	45
4.5.7	Conductivity	46
4.5.8	Total Dissolved Substances(TDS)	47
5	CONCLUSION AND RECOMMENDATION	49
	REFERENCES	50
	Appendices A-D	53-57

LIST OF TABLES

NO	TITLE	PAGE
1	Standard A and standard B	17
2	Composition of Membrane Dope Solutions	27
3	Viscosity for Dope Solution	32
4	Properties of Raw Refinery Wastewater Sample	35
5	Comparison Properties of Water Sample After Passed Through Between Silica Sand only and Activated Carbon only	36
6	Properties of Water Sample After Passed Through Combine Silica Sand And Activated Carbon	37

LIST OF FIGURES

NO	TITLE	PAGE
1	SEM cross section image of dialysis membrane produced without MSG.	10
2	SEM cross section image of dialysis membrane produced with 2% MSG	10
3	Flow diagram of the Methodology	26
4	Design of the Equipment	28
5	Graph of viscosity versus speed	39
6	Graph of Flow Rate versus Types of Membranes	40
7	Graph of Turbidity versus Types of Membranes	41
8	Graph of COD versus Types of Membranes	42
9	Graph of BOD versus Types of Membranes	43
10	Graph of pH versus Types of Membranes	44
11	Graph of sulfide versus Types of Membranes	45
12	Graph of Conductivity versus Types of Membranes	46
13	Graph of TDS versus Types of Membranes	47

LIST OF ABBREVIATIONS

MSG	Monosodium Glutamate
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
TDS	Total Dissolve Substances
H₂S	Hydrogen Sulfide
NTU	Naphelometric Turbidity Units
ppm	Part Per Million
rpm	Revolutions per Minutes

LIST OF APPENDICES

NO	TITLE	PAGE
A	Gantt Chart	53
B	Properties of the Dope Solutions	54
C	Properties of the Water Sample	55
D	Testing For Membrane Performances	57

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Petroleum refining involves the transformation of crude oil into final useful products such as gasoline, gas oil, kerosene and jet fuel, and petrochemical feed stocks. Petroleum refining uses relatively large quantities of water, especially for cooling systems, desalting water, stripping steam, and water used for flushing during maintenance and shut down. In addition, surface water runoff and sanitary wastewaters are accounted in the wastewater system. The quantity of wastewater generated and their characteristics depend on the process configuration. As a general rule, approximately 3.5–5 m³ of wastewater are generated per tone of crude oil processed when cooling water is recycled. (Mohamed and Walid,2006)

Wastewater, generated by the catalytic hydro cracking and refining of various crude-oil fractions, contains, in addition to hydrocarbons, large amounts of nitrogen and sulfur, in the form of ammonia and hydrogen sulfide (H₂S), respectively. (Eleni et al,2005). Several problems are related to sulfide buildup, these include corrosion of concrete sewer pipes, release of obnoxious odors to the urban atmosphere, safety hazards to sewer workers due to the toxicity of sulfide gas and negative impacts on the subsequent wastewater treatment. Typical refinery wastewaters may contain 1 or

2 mg L⁻¹ sulfide, but certain units, such as sour water strippers, may produce sulfide concentrations as high as 150 mg L⁻¹. (Levent and Hanife,2007).

H₂S, which is the most important form of sulfur, exists in equilibrium with bisulfide (HS⁻) and sulfide (S²⁻) in aqueous solution and can volatilize to H₂S gas. (Levent and Hanife,2007). H₂S is a highly toxic compound that can form in any aqueous system which contains both organic matter and sulfate. Such conditions are found in natural systems (e.g. the Black Sea) and can arise as a result of anthropogenic activities, including aqua cultural practices and the production of anaerobic sewage and industrial wastewaters (Simon et al,2001).

Several treatment technologies have been used to remove H₂S. They include scrubbers, bio-filters, incinerators, absorbers, ozonation processes. Currently, packed towers, mist scrubbers, and bio-filters are often used for the removal of H₂S and other off-gas odors. Limitations to the packed towers and the mist scrubbers are that H₂S is only removed from the areas where gas and liquid are properly contacted. In addition, it is very expensive to install and to maintain, requiring considerable spaces, and operating and maintenance costs. Proper control of liquid–gas flow rates must be carried out so as to optimize the operation. In order to obtain high removal efficiencies and low H₂S outlet concentration, multi-stage scrubbers are often needed. (Dongliang et al, 2002)

Nowadays , Membrane separation process used in water treatment minimizes waste and pollution unlike coagulation-clarification and ion exchange. It is becoming the technology of choice for making potable water around the world – desalination, reuse of municipal water, wastewater reclaim and recycle – as well as for pollution control treatment and zero discharge.(Rajindar,2006)

1.2 Problem Statement

According to a recent UN report (The New York Times, July 26,2005), more than a billion people lack access to safe water; polluted water contributes to the death of about 15 million children each year. The United Nations Educational Scientific and Cultural Organization (UNESCO) estimates that by the year 2050, between two and seven billion people will face water shortage. Further, it is estimated that the amount of water available per person will shrink by third during the next two decades. (Ranjindar,2006)

The separation of hydrogen sulfide (H_2S) is required for reasons of health, odors problems, safety and corrosives problems. It causes an irritating, rotten-egg smell above 1 ppm (1.4 mg m^{-3}), and at concentrations above 10 ppm the toxicological exposure limits are exceeded. (Janssen et al, 1999) In addition to the potential for corrosion following biological oxidation to sulphuric acid .Hydrogen sulfide (H_2S) is highly toxic to aquatic organisms at low concentrations, and has been the cause of mass fish mortality in aquaculture systems. (Simon et al,2001)

1.3 Objective

The proposed research was studied to achieve the following objectives:

1. To separate hydrogen sulfide (H_2S) from refinery wastewater treatment.
2. To treat the wastewater by using membrane.
3. To study the influence of composition on the membrane performance.

1.4 Scope of Study

In order to achieve the objective, several scopes have been drawn:

1. Preparing and casting membrane.
2. Fabricate equipment for wastewater treatment.
3. Determine the effect of composition on the membrane performance.
4. Determine the effectiveness of the membrane in separate H_2S gas from waste water .
5. Determine the effectiveness of membrane in wastewater treatment.

1.5 Rationale and Significance

Separate the H_2S from refinery wastewater by using hybrid membrane is beneficial to the environment and society. The benefits are:

1. Preventing the community from toxic and danger H_2S gas in refinery wastewater.
2. Preserving and protecting environment.
3. Reduce the cost and energy consumption to remove H_2S from refinery wastewater.
4. Ensure the wastewater can disposed safety in an environmentally acceptable manner.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane

There are a number of definitions of word ‘membrane’, which can vary considerably in comprehensiveness and clarity. Three definitions arbitrarily chosen from pertinent technique literature from the last 20 years are provided below:

- “An intervening phase separating two phases and /or acting as an active or passive barrier to the transport of matter between phases” –*The Europe Society of Membrane Science and Technology (Now The European Membrane Society)*
- “An inter phase separating two homogenous phases and affecting the transport of different chemical components in a very specific way”- *Prof.Heine Strathmann, former Head of Department of Membrane Technology, University of Twente.*
- “A material through which one type of substance can pass more readily than others, thus presenting the basis of separation process”- *Prof.George Solt, former Director of the school of water sciences, Cranfield.*

For the purposes of this discussion of membrane technology for wastewater treatment, Solt’s definition can be considered adequate: it is that property of the

membrane which permits the separation of component in and/or from water that is of key interest. (Simon and Bruce, 2003).

Since their first appearance two centuries ago, membranes have seen a great development in various industrial and fundamental science domains. Some authors consider that membrane technology reached its maturity in the early 1980s. Today, there is no doubt that the use of membrane processes is increasing in all fields. They are widely used in water desalination, wastewater treatment, the removal of heavy metal ions, nitrates, phosphates, pesticides, phenols and many other micro pollutants. The core of a membrane process is the membrane itself. Depending on the membrane nature and characteristics, a process (e.g. a pressure-driven or an electro-membrane process) and operating conditions are to be chosen. Among the processes, ultrafiltration has a large potential for applications in various fields: biotechnology, pharmacy and water treatment. The new development of applications relies on the availability of membranes having high permeability and high fouling and chemical resistances. Fouling resistance and high permeability would be obtained by improvements in the membrane hydrophilicity, while chemical resistance would come from the intrinsic properties of the polymer materials. (Chamekh et al, 2005)

Water scarcity problems have been more and more severe around the world and so great attention is being paid into reclamation and reuse of wastewater from municipalities and industrial plants. Membrane processes are thus increasingly popular for wastewater reuse applications, since they could play a key role in removing the complex components of dissolved and particulate matter contaminants in wastewater. A wide range of membrane processes from porous MF to dense reverse osmosis (RO) filtration has been employed for advanced wastewater treatment. (Suck and Kwang, 2003)

For instance, a large-scale RO plant treating secondary effluent at Water Factory 21, California, USA, has been in operation since 1994, whose permeate was used to recharge groundwater aquifers and so to prevent the intrusion of seawater. MF

was also considered as a pretreatment train of the RO system instead of existing physical–chemical treatment methods such as lime clarification and multimedia filtration. It was also reported that Eraring Power Station, Australia, installed a tertiary treatment system equipped with RO in combination with MF to produce treated water of high quality for planned non-potable reuse. Samsung Chemicals in Korea, has been operating an RO system for more than 15 years to obtain suitable quality of industrial water from a polluted river. Even RO filtration was considered for recycling space mission wastewater to produce potable and washing water because it is compact and easy to operate. And many more water-intensive industrial sectors such as textile, food, pulp and paper industries are interested in using membranes for wastewater repurification. (Suck and Kwang, 2003)

2.2 Hybrid membrane

A hybrid can be defined as (i) something of mixed origin or composition; (ii) something having two different types of components or aspects that produce similar functions or results ; or (iii) a composite formed or composed of heterogeneous elements . Hybrid systems represent a promising class of materials because they can potentially be used to control and obtain the appropriate ratio between hydrophilic and hydrophobic domains in order to have sufficient proton conductivity, mechanical strength and morphological stability simultaneously. Predictable improvements of membrane properties include higher thermal stability, stabilization of morphology, better mechanical properties and optimized water uptake . (Ahmad et al, 2010)

Hybrid microfiltration (MF) and ultrafiltration (UF) processes appear to be more attractive for wastewater treatment because they promise high fluxes at relatively low pressures. Use of the loose membranes has been often considered as a pretreatment step prior to sophisticated desalination or organic removal processes, in place of conventional clarification or sand filtration. (Suck and Kwang, 2003)

The term hybrid or integrated membrane processes also refers to the integration of one or more membrane process with or without conventional unit operations to increase performance depending on the type of feed and product quality required. The main goal of these system is to increase purity and productivity. Hybrid membrane system also reduce operating costs and environmental pollution, and make the overall process more efficient. (Rajindar,2006)

For the last 10 years, there was so many materials or filler had been tried to develop a new hybrid membrane with better quality such as silica , montmorillonite (MMT) , polyvinyl alcohol , SiO_2 , ZrO_2 , zeolite, zirconium phosphate , poly(propyleneoxide) , SPEEK , PBI , PSF and so many others. (Ahmad et al, 2010)

2.3 Membrane additive

The addition of organic or inorganic additives as the third component to the blend polymers has been one of the important procedures used in membrane preparation to control the morphology and performance of membranes. Studies have been conducted by adding additives such as polyethylene glycol (PEG), hyperbranched polyglycerol (HPG) polyvinylpyrrolidone (PVP) in the casting solution to improve the membrane performance. The presence of PEG in the dialysis membrane enhanced the membrane performance exhibited by the high urea clearance and high urea permeability. The effects of PVP on CA/PSF blend membranes and showed that increase in the concentration of PVP in casting solution resulted in the improved performance of membranes. Polysulfone (PSF) is widely used as an ultrafiltration, reverse osmosis and pervaporation membrane since polysulfone has good thermal and chemical stabilities. (G.Arthanareeswaran et al, 2009)

The effect of additives to the casting solution or bore liquid on the membrane structure depends on the extent of additives influence on the precipitation rate. If the additives in the casting solution increase the rate of precipitation, finger structure is favorable. But, if the additives, for instance benzene is present in the casting solution, it will tend to reduce the rate of precipitation and therefore favor a sponge structure. (Ani et al ,2009)

Effects of different additives such as water, glycerol, lithium per chlorate and ethanol on the PVDF membrane morphology. Their results showed that with increasing water into the casting solution, the macrovoids became smaller and appeared to be more regular. The membrane permeation flux also increased as more water was added, where at 4.6% water in the casting solution a flux increment to $1640 \times 10^{-5} \text{ L/m}^2 \text{ h Pa}$ ($1640 \text{ L/m}^2 \text{ h bar}$) was achieved. Furthermore, glycerol in the PVDF solution suppressed gelation induced by crystallization, whereas lithium salt enhanced the gelation behavior. fabricated porous polysulfone (PSF) membranes using propionic acid as an additive in the polymer solution and found that the precipitation rate of the polymer solution was enhanced significantly. The results revealed that membrane permeability increased near ten times with the addition of propionic acid in the PSf dope. In addition, compared to distilled water as an additive in the PVDF polymer dope, glycerol and phosphoric acid showed a larger pore size and a higher value of MWCO that improved the membrane permeability and CO_2 absorption flux . A high molecular weight additive like PVP can enhance phase separation of spinning solution. (A.Mansourizadeh and A.F Ismail,2009)

The addition of 5 wt.% PVP in 15 wt.% PSF solution enhanced demixing of solvent and non-solvent during membrane fabrication. It also improved the membrane permeate flux by a factor of one. However, further increment of PVP in the solution resulted in delayed demixing and the permeate flux decrease, which reveals that the thermodynamic enhancement is overtaken by the rheological hindrance in demixing of the solution. (A.Mansourizadeh and A.F Ismail,2009)

The SEM cross section image of the dialysis membrane produced without any additives. A dense spongy structure without the presence of any macro void is observed. The addition of 2 wt% MSG apparently promotes the formation of macrovoids within the support layer as depicted in Figure below. (Ani et al ,2009)

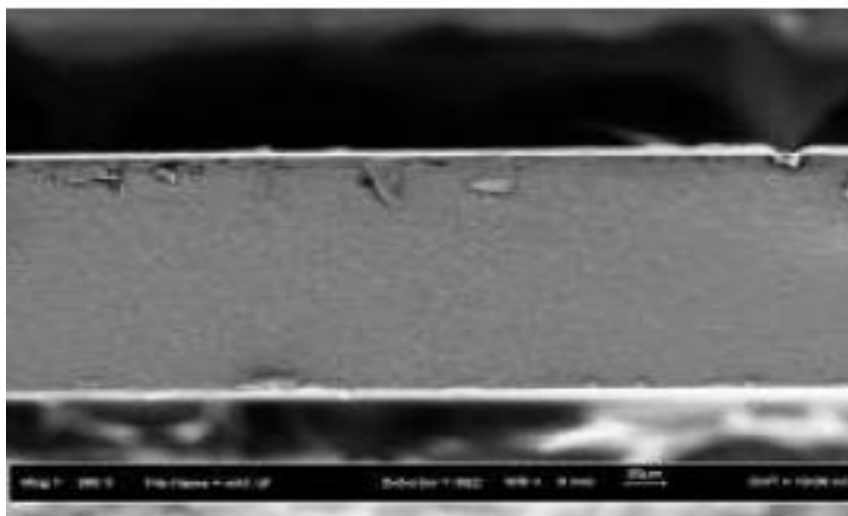


Figure 1:SEM cross section image of dialysis membrane produced without MSG

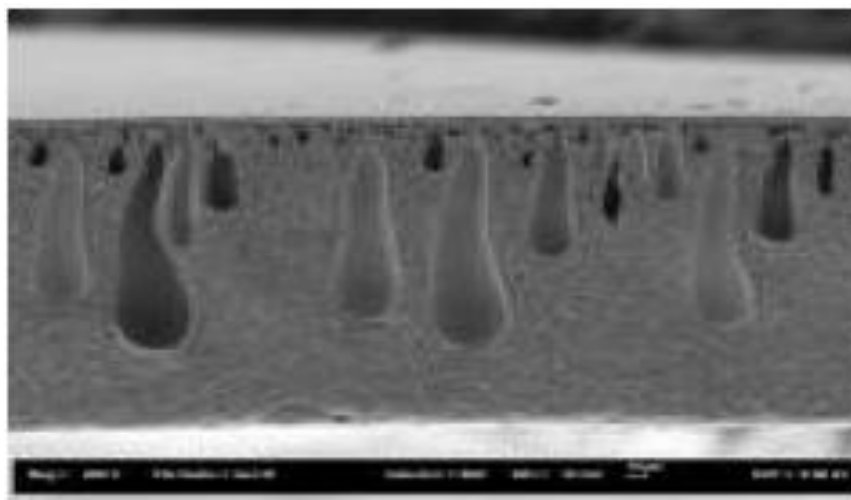


Figure 2:SEM cross section image of dialysis membrane produced with 2% MSG

Apparently the addition of MSG does not only affect the performance of membranes but also has an influence on both the morphology of membranes. A very dense spongy structure is observed when no MSG is used. However, small amounts of MSG (1 wt% to 6 wt%) added seem to promote instantaneous demixing forming finger like structure which seems to be favorable in dialysis membranes. The MSG seems to encourage the mechanism of phase inversion transit from delayed demixing to instantaneous demixing, consequently promotes the formation of macrovoids and finger like structures. On the contrary, when high amounts of MSG (8 wt%) was added into the casting solution, MSG seems to promote delayed demixing, hence the spongy structure is obtained. (Ani et al ,2009)

The occurrences of macrovoid can be explained by nucleation theory where macrovoids formation is dominated by the ratio of influx of the coagulant liquid (nonsolvent) and the influx of solvent from casting solution into the nonsolvent droplet in casting solution. It is possible that MSG in casting solution promotes the formation of nuclei with high solvent concentration. Thus, the size and the number of macrovoids increased as the amount of MSG increased in casting solution. However, when the concentration of additives was too high, the viscosity of dope solution increased. Hence, when concentration of additive goes beyond 6 wt%, the influx of the solvent (formic acid) from polymer solution into the nonsolvent droplet decreased. The absence of nuclei with high solvent concentration promotes the spongy like structure. (Ani et al ,2009)

2.4 Ultrafiltration (UF) membrane

Ultrafiltration is a pressure-driven membrane separation process for separation of macromolecules from liquid solutions. The working pressure provides the

driving potential to force the solvent and the small molecules to flow through the membrane while the macromolecules are rejected. The concentration of the rejected solute on the membrane surface is always higher than that in the bulk solution that is called concentration polarization phenomenon. (Tung and Li,2006)

Ultrafiltration membrane operates at very low pressure, typically between 2 and 5 bar, Further, due to the larger pores in the membrane skin, the UF membranes have an order of magnitude higher flux than reverse osmosis (RO) membranes. UF membranes separation depends upon membrane pore size, solute-membrane interactions, shape and size of the macromolecule, and concentration polarization. (Rajindar,2006)

The UF membranes are manufactured by the phase-inversion process. The most widely used polymer is polysulphone (PS), but increasingly other polymers are being used; cellulose acetate (CA),poly ether sulphone (PES), polyacrylonitrile (PAN) , and poly vinylidene fluoride (PVDF) polymers. (Rajindar,2006)

Industrial UF was developed primarily for the treatment of wastewater to remove particulate and macromolecular matter to meet the municipal effluent discharge standards and to recover valuable component for recycle.. Since the early 1990s, UF hollow fibre membrane systems have been used in a variety of municipal water treatment application, including treatment of surface water for production of safe drinking water and advanced tertiary treatment of municipal wastewater for recovery and reuse. UF membranes remove very small size contaminants in feed water , including essentially all of the suspended solids, colloidal particles and large size microorganisms.(Rajindar,2006)

2.5 Hydrogen Sulfide (H₂S)

Identity

CAS no.: 7783-06-4

Molecular formula: H₂S

Physicochemical properties [Conversion factor in air: 1 mg/m³ = 0.670 ppm]

Property Value

Physical appearance Colourless gas

Melting point -85.5 °C

Boiling point -60.7 °C

Density 1.54 g/litre at 0 °C

Water solubility 4370 ml/litre at 0 °C; 1860
ml/litre at 40 °C

Vapour pressure 1875 kPa at 20 °C

Hydrogen sulfide (H_2S) has an offensive "rotten eggs" odour that is detectable at very low concentrations in air, below $8 \mu\text{g}/\text{m}^3$. At concentrations of 50–150 mg/m^3 in air, it has a deceptively sweet smell; above this range, it deadens the sense of smell. In water, the taste and odour thresholds for hydrogen sulfide are estimated to be between 0.05 and 0.1 mg/litre . The taste and odour threshold for sulfides is about 0.2 mg/litre . (WHO,2003)

The major uses of hydrogen sulfide (H_2S) include its conversion into sulfur and sulfuric acid and the manufacture of inorganic sulfides, thiophenes, thiols, thioaldehydes, and thioketones. It is used in dye manufacturing, tanning, the production of wood-pulp, chemical processing, and the manufacture of cosmetics. Spring waters that contain elevated concentrations of hydrogen sulfide are used for therapeutic medicinal baths. (WHO,2003)

Hydrogen sulfide (H_2S) is formed when soluble sulfides are hydrolysed in water. In water, hydrogen sulfide dissociates, forming monohydrogensulfide (HS^-) and sulfide (S^{2-}) ions. The relative concentrations of these species are a function of the pH of the water, hydrogen sulfide concentrations increasing with decreasing pH. At pH 7.4, about one-third exists as undissociated hydrogen sulfide and the remainder largely as the monohydrogensulfide anion. The sulfide is present in appreciable concentrations above pH 10. In well aerated water, hydrogen sulfide is readily oxidized to sulfates and

biologically oxidized to elemental sulfur. In anaerobic water, microbial reduction of sulfate to sulfide can occur. (WHO,2003)

Hydrogen sulfide (H_2S) is present in air primarily as a result of natural emissions. Concentrations generally vary from 0.1 to 1 $\mu\text{g}/\text{m}^3$ in ambient air, although concentrations above 100 $\mu\text{g}/\text{m}^3$ have been reported near industrial plants. An estimated daily intake of 2–20 μg can be calculated on the assumption that 20 m^3 of air containing hydrogen sulfide at natural concentrations is inhaled. (WHO,2003)

Most of the hydrogen sulfide (H_2S) present in raw waters is derived from natural sources and industrial processes. It is particularly noticeable in some groundwaters, depending on source rock mineralogy and microorganisms present. In the USA, a maximum concentration of 500 μg of undissociated hydrogen sulfide per litre has been reported in fresh water. (WHO,2003)

A number of foodstuffs and drinks may contain sulfides. However, estimation of exposure from food is complicated by the formation of sulfides in cooked foods. Levels in heated dairy products range from 0.8 mg/litre in skimmed milk (0.1% fat) to 1.84 mg/litre in cream (30.5% fat). The hydrogen sulfide content of cooked meat ranges from 0.276 mg/kg for beef to 0.394 mg/kg for lamb. Hydrogen sulfide is formed principally from the sulfur-containing amino acids in meat protein, levels being higher in anaerobically packaged meat. Dimethyl sulfide is used in the manufacture of jellies, candy, soft drinks, and cream in the United Kingdom, where the maximum probable intake has been estimated at 1.7 mg/day .(WHO,2003)

Hydrogen sulfide (H_2S) is a highly toxic colorless gas with an unfavorable reputation, particularly from a physiological standpoint. Exposure to this broad spectrum toxicant can have serious health ramifications, the majority of which have been identified under conditions of acute, high concentration exposure. The deleterious effects of H_2S have been recognized in a myriad of natural and industrial settings,

including the oil and gas industry, where the vast majority of exposures occur (Arnold et al., 1985; Burnett et al, 1977).

Under natural conditions, H_2S is produced during the decomposition of organic protein (Roth, 1993). Natural sources of H_2S include volcanic gases, sulphur springs, crude petroleum, and natural gas. H_2S is also released into the environment as a by-product of certain industrial operations (Beauchamp et al., 1984). Industrial sources of H_2S include sewage treatment facilities, oil refineries, food processing operations, natural gas plants, and mining (Milby, 1962).

Hydrogen sulfide (H_2S), as a highly undesirable contaminant, is produced in association with some industrial processes, such as gas streams from wastewater treatment, food processing, petroleum refining, tanneries, paper and pulp manufacturing and solid waste processing plants

Hydrogen sulfide (H_2S) is a toxic gas and is also one of the major causes for odor problems in domestic wastewater treatment plants and in other chemical or petrochemical industries. It not only causes the nuisance, but also has serious health effects associated with exposure of H_2S . Short time exposure at high concentration of several tens of ppm can have dramatic health effect. Long time exposure at the very low level of less than 1 ppm can also cause health effect. In addition, H_2S is a toxic component for many catalytic reaction processes. (Dongliang et al, 2002)

Exposure to high concentrations of H_2S , albeit for brief durations, is extremely toxic to humans. Symptoms of exposure under these conditions range from minor irritative effects (e.g. “gas eye”) to coma, or even death, subsequent to paralysis of the brainstem medullar respiratory centre. A preponderance of nervous system sequelae characterize the clinical picture in those fortunate enough to survive H_2S “knockdown”. (L. A. Partlo et al, 2001)

No data are available on the oral toxicity of hydrogen sulfide. However, alkali sulfides irritate mucous membranes and can cause nausea, vomiting, and epigastric pain

following ingestion. The oral dose of sodium sulfide fatal to humans has been estimated at 10–15 g. (WHO,2003)

When inhaled, hydrogen sulfide is highly acutely toxic to humans. Its rapid mode of action involves the formation of a complex with the iron(III) ion of the mitochondrial metalloenzyme cytochrome oxidase, thereby blocking oxidative metabolism . Other enzymes reported to be inhibited by sulfides are succinate dehydrogenase, adenosinetriphosphatase, DOPA oxidase, carbonic anhydrase, dipeptidase, benzamidase, and some enzymes containing iron such as catalase and peroxidases. Reduction of disulfide bridges in proteins has been suggested as a mechanism whereby enzyme function could be altered. Irritation of the eyes and respiratory tract can be observed at concentrations of 15– 30 mg/m³, and concentrations of 700–1400 mg/m³ can cause unconsciousness and respiratory paralysis resulting in death. (WHO,2003)

Few studies on prolonged exposure to low concentrations of hydrogen sulfide have been undertaken. In one study, the reticulocytes of 17 workers engaged in wood-pulp production who were exposed to low levels of hydrogen sulfide and methylthiols were analysed. The activities of a number of enzymes involved in the haem biosynthetic pathway were inhibited, although the mechanism is unclear. (WHO,2003)

2.6 Standard A and standard B

Table 1 show the discharge permits which were outlined by the Department of Environment Malaysia (DOE).

Table 1: Standard A and standard B

	Parameters	Units	Standards	
			A	B
1	Temperature	⁰ C	< 40.0	< 40.0
2	pH	pH	6.0 – 9.0	5.5 – 9.0
3	BOD ₅ at 20 °C	mg/L	< 20.0	< 50.0
4	COD	mg/L	< 50	< 100
5	Suspended Solids	mg/L	< 50	< 100
6	Mercury	mg/L	< 0.005	< 0.05
7	Cadmium	mg/L	< 0.01	< 0.02
8	Chromium, Hexavalent	mg/L	< 0.05	< 0.05
9	Arsenic	mg/L	< 0.05	< 0.10
10	Cyanide	mg/L	< 0.05	< 0.10
11	Lead	mg/L	< 0.10	< 0.50
12	Chromium, trivalent	mg/L	< 0.20	< 1.00
13	Copper	mg/L	< 0.20	< 1.00
14	Manganese	mg/L	< 0.20	< 1.00
15	Nickel	mg/L	< 0.20	< 1.00
16	Tin	mg/L	< 0.20	< 1.00
17	Zinc	mg/L	< 2.00	< 2.00
18	Boron	mg/L	< 1.00	< 4.00
19	Iron	mg/L	< 1.00	< 5.00
20	Phenol	mg/L	< 0.001	< 1.000
21	Chlorine, Free	mg/L	< 1.00	< 2.00
22	Sulphide	mg/L	< 0.50	< 0.50
23	Oil & Grease	mg/L	Not Detectable	10.0